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Structural and Stereodynamic Studies on Molecular Early Transition Metal Derivatives. 3. Molecular Structure of Trichlorooxobis(hexamethylphosphorotriamide)niobium(V)

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The structure of $NbOCl_3(HMPA)_2$ (HMPA = $OP(NMe_2)_3$) has been determined by x-ray crystallography. The compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 8.591$ (2) Å, $b = 19.912$ (5) Å, $c = 15.133$ (4) Å, $\beta = 99.51$ (2)°, and $Z = 4$. The structure refined to a final residual $R = 0.044$. The metal atom is hexacoordinated with the two HMPA ligands occupying cis positions in a meridional isomer. The coordination polyhedron is a distorted octahedron as a result of the strong electronic repulsion of the oxo bond toward its neighboring bonds. A notable lengthening (0.19 Å) is observed for the Nb–O coordination bond trans to the oxo bond. It is interesting to note that this difference does not significantly affect the P═O bond distances but is manifested in appreciable differences in the P—N bond lengths.

Introduction

Although the coordination chemistry of the niobium(V) oxohalides has been the subject of extensive investigation, which has resulted in the preparation of numerous adducts,[1] there is still very little structural information available on these compounds. We have recently reported an NMR study of the molecular constitution, solution equilibria, and stereodynamic behavior of solutions of some niobium oxochloride adducts of type $NbOCl_3L_2$ (L = $OSMe_2$ or $OP(NMe_2)_3$ ((HMPA)).[2] It was found that the solutions of $NbOCl_3(HMPA)_2$, for example, consist of complex mixtures of monomeric species having ligand:metal stoichiometries of 1:1, 1:2, and 1:3. Each of these stoichiometries has several isomers in dynamic equilibrum on the NMR time scale, the relative abundance of the various species being highly dependent on the nature of the solvent and on the concentration. However, the meridional isomer of $NbOCl_3(HMPA)_2$, in which the ligands occupy cis positions, was always predominant.

To date, x-ray diffraction studies have been limited to two adducts with nitrogen donors, namely $NbOCl_3(MeCN)_2$[3] and $NbOCl_2(OEt)$bpy,[4] in which the ligands were found to occupy cis positions.

We now report the x-ray structure determination of $NbOCl_3(HMPA)_2$. It was undertaken in order to compare the molecular structure in the solid state with that found by ^1H NMR in solution and to gain information concerning the trans effect caused by the oxo bond and the HMPA ligands. Also there is still no x-ray structure determination available on HMPA, and the only structures reported on its adducts are $UCl_4(HMPA)_2$[5] and $MoO_5(HMPA)L$[6] where L = py or H_2O; only in the latter cases have all the nonhydrogen atoms been located. It thus seemed desirable to obtain more data on this common ligand, which could be discussed in relation to its donor properties.

Experimental Section

Crystals of $NbOCl_3[OP(NMe_2)_3]_2$ suitable for x-ray diffraction analysis were obtained through an oxygen vs. chlorine exchange reaction between $NbCl_2(OCH_3)_3$ and a threefold excess of the ligand in CH_2Cl_2 (3 M) at room temperature.[7] The crystals grew when the reaction mixture was allowed to stand for 1 day at −30 °C.

Crystal Data. An irregular crystal chip with approximate dimensions 0.40 × 0.20 × 0.15 mm was mounted in a Lindemann tube under dry argon. The unit cell was determined to be monoclinic with the following cell dimensions measured on the diffractometer: $a = 8.591$ (2), $b = 19.912$ (5), $c = 15.133$ (4) Å; $\beta = 99.51$ (2)°; $Z = 4$. The density $d = 1.53$ g cm^{-3} was measured by flotation in a mixture of $CFCl_2CF_2Cl$ and ether ($d_{calcd} = 1.49$ g cm^{-3} for $Z = 4$).[8] The space group was determined to be $P2_1/n$ by systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$).

Crystallographic Procedures. The intensities of 3362 unique reflections, of which 812 were less than the 3σ limit, were measured with a Syntex $P2_1$ automated diffractometer using filter monochromated Mo Kα radiation and a profile interpretation technique[9] to a maximum of $(\sin \theta)/\lambda = 0.540$ Å^{-1} and operating in the scan mode θ–2θ (range 2°). No absorption correction was applied ($\mu = 9.20$ cm^{-1}). Scattering factors for the neutral atoms and anomalous dispersion factors for Nb, Cl, and P atoms were taken from literature sources.[10] All computer programs were taken from the "X-Ray 72" program system.[11] Figure 1 was drawn using program ORTEP.[12]

Solution of the Structure. The position of the niobium atom was found from the interpretation of a three-dimensional Patterson map. A difference Fourier synthesis phased with the niobium atom alone revealed all of the medium and most of the light nonhydrogen atoms. Inclusion of these atoms in the model, followed by a further difference Fourier synthesis, led to the location of the remaining nonhydrogen atoms. The resulting structure was refined on the structure factors $|F|$ by block-matrix least squares to a final residual $R = 0.044$ ($R_w = 0.055$); the goodness of the fit was 3.26. In the early cycles all of the atoms were allowed to vibrate isotropically, and in the later cycles anisotropic temperature factors were refined. In a final cycle, isotropic extinction was refined following the method of Zachariasen[13] and shown to be negligible. The weights used were $1/\sigma^2$ where the esd's (σ) of the structure factors were derived from counting statistics and the variation in the intensities of the periodically measured check reflections. The number of observations per refined parameter was 12 (a compilation of observed and calculated structure factors is available as supplementary material).

Results and Discussion

The atomic coordinates are listed in Table I, and the calculated bond lengths and angles are presented in Table II. A perspective drawing of the molecule is presented in Figure 1. The adduct is monomeric as in solution, with the hexacoordinated metal atom octahedrally surrounded by one oxygen and three chlorine atoms and by two HMPA ligands. These two ligands are cis to each other, one of them being trans to the oxo bond; this is the geometrical isomer which was always predominant in solution.

The Nb═O distance (1.692 (5) Å) is very close to those found for $NbOCl_3(MeCN)_2$[3] and $NbOF_5^{2-}$ (1.68 (2) Å) or for $NbOCl_2(OEt)$bpy (1.71 (3) Å)[4] but slightly shorter than the distance obtained in $NbO(S_2CNEt_2)_3$ (1.74 (1) Å)[15] and is consistent with a niobium–oxygen multiple bond.[16]

More striking is the fact that the various distinct niobium–chlorine bonds, i.e., those trans to the HMPA and those trans to each other, have comparable lengths (2.399 (2) and 2.417 (2) Å). In both cases they are longer than the sum of the covalent radii (2.33 Å); they are also longer than those measured for the terminal Nb–Cl bonds in $(NbCl_5)_2$ (2.250 (6) and 2.302 (5) Å)[17] and in $NbOCl_3(MeCN)_2$ (2.313

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Table I. Atomic Parameters for $NbOCl_3(HMPA)_2$ with Standard Deviations in Parentheses

Atom	x	y	z	U_{11} $(U)^a$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb	0.09580 (8)	0.17434 (3)	0.19851 (5)	0.0372 (4)	0.0285 (3)	0.0336 (4)	−0.0001 (4)	0.0030 (3)	−0.0002 (3)
Cl1	0.3759 (2)	0.1868 (1)	0.2423 (2)	0.045 (1)	0.059 (1)	0.079 (2)	−0.013 (1)	0.011 (1)	−0.005 (1)
Cl2	0.1254 (3)	0.1546 (1)	0.0459 (1)	0.083 (2)	0.068 (2)	0.040 (1)	0.006 (1)	0.019 (1)	0.005 (1)
Cl3	−0.1758 (2)	0.1379 (1)	0.1638 (1)	0.038 (1)	0.056 (1)	0.057 (1)	0.001 (1)	−0.004 (1)	−0.006 (1)
O1	0.0563 (7)	0.2575 (2)	0.1831 (4)	0.070 (4)	0.030 (3)	0.077 (4)	0.003 (3)	−0.002 (4)	0.003 (3)
O2	0.1455 (5)	0.0647 (2)	0.2226 (3)	0.038 (3)	0.024 (2)	0.041 (3)	0.002 (2)	0.007 (2)	0.001 (2)
O3	0.0742 (5)	0.1681 (2)	0.3310 (3)	0.036 (3)	0.044 (3)	0.032 (3)	0.005 (3)	0.002 (2)	−0.010 (2)
P1	0.2272 (2)	−0.00096 (9)	0.2186 (1)	0.034 (1)	0.027 (1)	0.035 (1)	0.0005 (9)	0.0058 (9)	−0.0003 (9)
P2	0.0041 (2)	0.19246 (9)	0.4103 (1)	0.035 (1)	0.037 (1)	0.031 (1)	0.0013 (9)	0.004 (1)	−0.0039 (9)
N1	0.0930 (7)	−0.0604 (3)	0.2133 (4)	0.043 (4)	0.024 (3)	0.079 (5)	−0.009 (3)	0.008 (4)	−0.003 (3)
N2	0.3239 (7)	−0.0138 (3)	0.1348 (4)	0.046 (4)	0.040 (4)	0.044 (4)	0.006 (3)	0.016 (3)	−0.001 (3)
N3	0.3634 (7)	−0.0081 (3)	0.3083 (4)	0.047 (4)	0.044 (4)	0.040 (4)	0.003 (3)	−0.008 (3)	0.006 (3)
N4	−0.0734 (8)	0.2658 (3)	0.3992 (4)	0.061 (5)	0.043 (4)	0.044 (4)	0.015 (4)	0.009 (4)	−0.010 (3)
N5	−0.1376 (8)	0.1418 (3)	0.4242 (5)	0.048 (4)	0.052 (4)	0.066 (5)	−0.010 (4)	0.020 (4)	−0.006 (4)
N6	0.1482 (8)	0.1925 (3)	0.4950 (4)	0.066 (5)	0.065 (5)	0.028 (4)	0.000 (4)	−0.003 (4)	−0.009 (3)
C1	−0.0770 (9)	−0.0478 (4)	0.1969 (6)	0.023 (5)	0.055 (6)	0.105 (8)	−0.005 (4)	0.012 (5)	−0.013 (5)
C2	0.139 (1)	−0.1326 (4)	0.2139 (7)	0.067 (7)	0.023 (5)	0.129 (9)	−0.001 (4)	0.017 (6)	−0.000 (5)
C3	0.470 (1)	0.0250 (4)	0.1323 (6)	0.051 (6)	0.064 (6)	0.083 (7)	−0.007 (5)	0.037 (5)	0.004 (5)
C4	0.232 (1)	−0.0305 (4)	0.0461 (5)	0.078 (7)	0.077 (6)	0.029 (5)	0.016 (5)	0.001 (5)	−0.012 (4)
C5	0.344 (1)	0.0282 (4)	0.3910 (5)	0.081 (7)	0.075 (6)	0.033 (5)	0.003 (6)	−0.005 (5)	−0.011 (5)
C6	0.486 (1)	−0.0624 (4)	0.3192 (6)	0.063 (6)	0.057 (6)	0.086 (8)	0.027 (5)	−0.018 (6)	0.002 (5)
C7	0.001 (1)	0.3269 (4)	0.4418 (7)	0.084 (7)	0.047 (6)	0.123 (9)	−0.021 (6)	0.018 (7)	−0.029 (6)
C8	−0.212 (1)	0.2783 (5)	0.3284 (6)	0.074 (7)	0.087 (7)	0.066 (7)	0.047 (6)	−0.012 (6)	−0.006 (5)
C9	−0.274 (1)	0.1609 (5)	0.4692 (8)	0.068 (7)	0.088 (8)	0.13 (1)	−0.010 (6)	0.068 (7)	−0.020 (7)
C10	−0.131 (1)	0.0706 (4)	0.3988 (7)	0.103 (8)	0.034 (5)	0.116 (9)	−0.023 (5)	0.048 (7)	−0.018 (5)
C11	0.315 (1)	0.2072 (5)	0.4859 (6)	0.031 (5)	0.123 (8)	0.063 (7)	−0.004 (5)	−0.007 (5)	−0.023 (6)
C12	0.113 (1)	0.1907 (6)	0.5869 (6)	0.104 (9)	0.16 (1)	0.033 (6)	−0.021 (8)	0.004 (6)	−0.003 (6)

[a] The expression for the temperature factors has the form $\exp(-T)$ where $T = 2\pi^2\Sigma h_i h_j U_{ij} a_i^* a_j^*$ for anisotropic atoms.

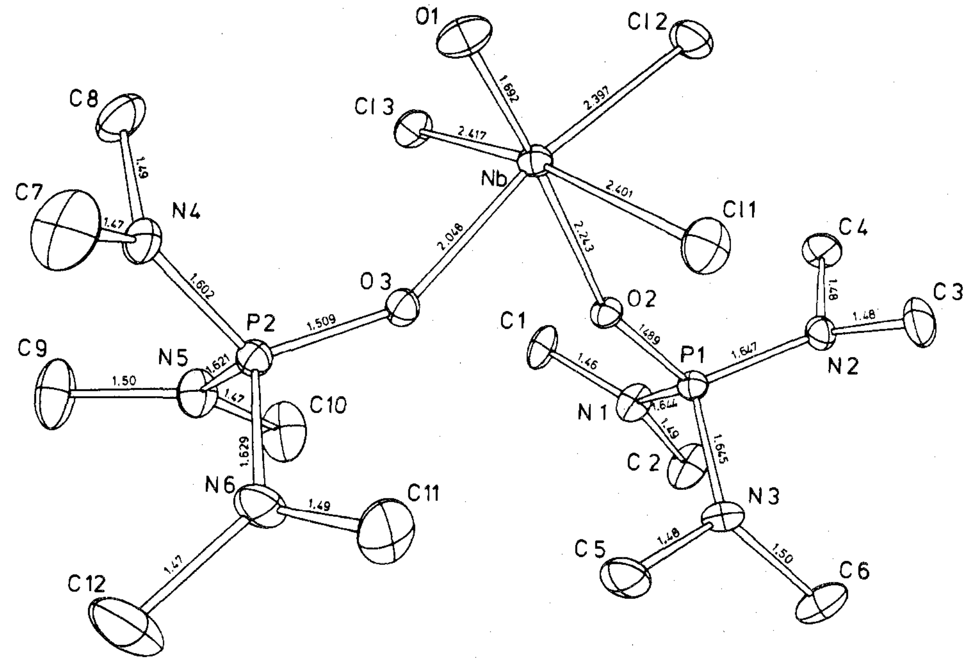

Figure 1. ORTEP view of $NbOCl_3(HMPA)_2$ with bond lengths (Å) and angles (deg).

(9)–2.377 (8) Å).[3] This may be rationalized on the basis of the electronic repulsion between the oxo bond and its neighboring bonds. Such a repulsion can be reduced either by a distortion of the coordination polyhedron and/or by a lengthening of the Nb–Cl bonds. An angular distortion is indeed found in this compound, as shown (Figure 2) by the inclination of the four equatorial bonds toward the ligand trans to the oxo bond, which results in a displacement of the metal 0.25 Å out of the equatorial plane. As a result the three chlorine atoms are maintained at the same distance from the terminal oxygen. However, the tendency of the oxo bond to repel its surrounding bonds is somewhat opposed by the steric requirements of the bulky HMPA ligands, and the angular distortion it causes is indeed slightly smaller than that observed in $NbOCl_3(MeCN)_2$, where the ClNbCl angle for the chlorine atoms trans to each other is 159.1 (2)°, as compared with 168.14 (8)° for the HMPA adduct. One may consider that,

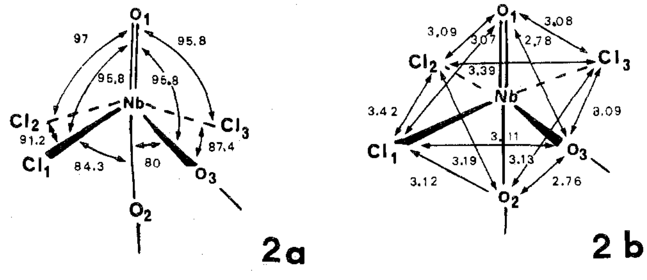

Figure 2. Coordination polyhedron of $NbOCl_3(HMPA)_2$: (a) angular distortion (deg); (b) contact distances (Å).

Table II. Bond Lengths (Å) and Angles (deg) for $NbOCl_3(HMPA)_2$ with Standard Deviations in Parentheses

Coordination Polyhedron			
Distances			
Nb-C1	2.401 (2)	Nb-O1	1.692 (5)
Nb-C2	2.397 (2)	Nb-O2	2.243 (4)
Nb-C3	2.417 (2)	Nb-O3	2.048 (5)
Angles			
Cl1-Nb-Cl2	91.23 (9)	Cl3-Nb-O1	95.8 (2)
Cl1-Nb-Cl3	168.14 (8)	Cl3-Nb-O2	83.9 (1)
Cl1-Nb-O1	95.8 (1)	Cl3-Nb-O3	87.4 (1)
Cl1-Nb-O2	84.3 (1)	O1-Nb-O2	175.9 (2)
Cl1-Nb-O3	89.1 (1)	O1-Nb-O3	95.8 (2)
Cl2-Nb-Cl3	89.64 (8)	O2-Nb-O3	80.0 (2)
Cl2-Nb-O1	97.0 (1)	Nb-O2-P1	157.8 (3)
Cl2-Nb-O2	87.1 (1)	Nb-O3-P2	150.6 (3)
Cl2-Nb-O3	167.0 (1)		
Ligands Trans to the Nb=O			
Distances			
O2-P1	1.489 (5)	N1-C2	1.49 (1)
P1-N1	1.644 (6)	N2-C3	1.48 (1)
P1-N2	1.647 (7)	N2-C4	1.48 (1)
P1-N3	1.645 (6)	N3-C5	1.48 (1)
N1-C1	1.46 (1)	N3-C6	1.50 (1)
Angles			
O2-P1-N1	107.5 (3)	C1-N1-C2	115.0 (6)
O2-P1-N2	117.9 (3)	P1-N2-C3	118.5 (5)
O2-P1-N3	108.6 (3)	P1-N2-C4	118.3 (5)
N1-P1-N2	106.8 (3)	C3-N2-C4	114.9 (7)
N1-P1-N3	112.1 (3)	P1-N3-C5	119.5 (5)
N2-P1-N3	104.0 (3)	P1-N3-C6	123.0 (5)
P1-N1-C1	123.9 (5)	C5-N3-C6	115.7 (6)
P1-N1-C2	120.6 (5)		
Ligands Trans to the Nb-Cl			
Distances			
O3-P2	1.509 (5)	N4-C8	1.49 (1)
P2-N4	1.602 (6)	N5-C9	1.50 (1)
P2-N5	1.621 (7)	N5-C10	1.47 (1)
P2-N6	1.629 (6)	N6-C11	1.49 (1)
N4-C7	1.47 (1)	N6-C12	1.47 (1)
Angles			
O3-P2-N4	115.1 (3)	C7-N4-C8	114.4 (6)
O3-P2-N5	108.0 (3)	P2-N5-C9	124.2 (6)
O3-P2-N6	106.0 (3)	P2-N5-C10	120.2 (6)
N4-P2-N5	105.8 (3)	C9-N5-C10	115.5 (7)
N4-P2-N6	109.3 (3)	P2-N6-C11	122.9 (5)
N5-P2-N6	112.8 (3)	P2-N6-C12	119.8 (6)
P2-N4-C7	124.5 (5)	C11-N6-C12	116.2 (7)
P2-N4-C8	119.5 (5)		

as a consequence, the constraint caused by the oxo bond in the latter case is also partially relieved by a lengthening of the Nb–Cl bonds (2.405 (2) Å average, as compared with 2.346 (8) Å average in the MeCN adduct).

Also noteworthy are the relatively small value of the O_3NbO_2 angle (80.0 (2)°) and the relatively small intermolecular O_2--O_3 contact (2.763 (6) Å as compared with 2.80 Å for the sum of the van der Waals radii). A comparable situation was observed in the $NbOCl_3(MeCN)_2$ adduct (NNbN = 89.4°; N--N = 2.96 Å instead of 3.0 Å). That the cis configuration of the ligands is formed despite some steric hindrance is a common feature for metals in the d^0 configuration and corresponds to the best utilization of the empty metal orbitals.[16]

Whereas no trans effect can be detected from the Nb–Cl bond lengths, an important effect is found for the metal–ligand bonds; the distance from the metal to the oxygen of the HMPA trans to the oxo bond is much longer (2.243 (4) Å) than that to the oxygen trans to chlorine (2.048 Å). This is in agreement with the idea that in quasi-octahedral complexes the trans weakening of an M–L bond should increase with the multiplicity and covalent character of the bond in the trans position.[16] The length of the Nb–O(P) bond trans to a chlorine atom is slightly less than the sum of the covalent radii (2.048 (5) vs. 2.07 Å). The MOP angles are large, 157.8 (3)° for the ligand trans to the oxo ligand and 150.6 (3)° for the one trans to chlorine, and comparable to those found for $MoO_5(HMPA)py$ (158.6 (3)°).[6]

It is noteworthy that, although the two Nb–O bonds have substantially different bond lengths, the P–O bond lengths are not very different (1.489 (5) and 1.509 (5) Å) and are comparable to the 1.51-Å bond length predicted for the free ligand on the basis of CNDO/2 calculations.[18] This suggests that, although there is a larger electron donation by the HMPA trans to chlorine, the P–O bond order remains constant. A reasonable mechanism to explain this observation would be that the difference in the ligand–metal bonds is transmitted to the p_π–d_π character of the P–N bonds. This means that a larger electron donation for the HMPA trans to chlorine is compensated by an increased electron donation from the nitrogen to maintain the P–O bond-order constant.[19] This hypothesis is supported by the observation that the P–N distances in the ligand trans to chlorine are all shorter than in the ligand trans to the oxo bond (average 1.617 (6) and 1.645 (6) Å, respectively) and in both cases are shorter than predicted from CNDO/2 calculations for the free ligand (1.69 Å) or from the sum of the covalent radii (1.80 Å). The average sum of the angles about the nitrogen atoms is 358°, thus indicating that the nitrogen atoms have essentially planar configurations, which is consistent with the above discussion.

No short intermolecular contacts were observed between the various molecules in the unit cell.

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Registry No. $NbOCl_3(HMPA)_2$, 62742-10-3.

Supplementary Material Available: Listings of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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